PREFACE

This Solutions Manual accompanies the text R. J. Silbey, R. A. Alberty, and M. G. Bawendi, PHYSICAL CHEMISTRY, Fourth Edition, John Wiley and Sons, Inc., Hoboken, NJ. The textbook has two types of problems at the end of each chapter. In addition to the usual problems that can be solved using a hand-held calculator, there are Computer Problems that require a personal computer with a mathematical application. The problems of the first type are divided into two nearly equivalent lists. The answers to problems in the first list are given in the back of the textbook, but the answers to problems in the second list are not. The answers to the Computer Problems are also not given in the textbook.

This Solutions Manual provides three types of information about the problems:

(1) Worked-out solutions are provided for problems in the first list of problems that can be solved using a hand-held calculator.

(2) Answers are given for problems in the second list that can be solved using a hand-held calculator.

(3) Solutions are provided in Mathematica™ (Wolfram Research, Inc., 100 Trade Center Drive, Champaign, Illinois 61820-7237) for all 170 problems that require a personal computer with a mathematical application. These solutions in digital form can be obtained from the web at http://www.wiley.com/college/silbey. In order to run these programs it is necessary to have Mathematica 5.0 installed in your computer. Each problem is in a separate Mathematica notebook.

The first section of the Solutions Manual contains the first two types of information, and the second section, which has been typed in Mathematica, contains the Mathematica programs and printouts. You can type the Mathematica programs in yourself or get them in digital form from the web, but in either case you are encouraged to modify the programs to make them apply to other substances, temperature ranges, values of physical properties, etc. The second section of this Solutions Manual also provides a ReadMe, an Introduction to Mathematica, and an Index of Mathematica Commands.

The solutions in Mathematica provide a kind of extension to the Examples in the textbook that can profitably be studied, whether you have a computer with a mathematical application or not. That is, an interesting problem is stated, an indication is given as to how to go about solving it, and the solution is given. In about 100 of the problems the solution is expressed by a 2D or 3D plot. You have already seen some of these plots in the textbook. These problems can also be solved with other mathematical programs, such as MathCad, MATLAB, and MAPLE.

Working problems is an important part of learning physical chemistry. Not all knowledge of physical chemistry is quantitative, but much of it is. Since physical chemistry utilizes physics and mathematics to predict and interpret chemical phenomena, there are many opportunities to use quantitative methods. In solving problems it is important to develop the habit of using units and canceling them to obtain the units for the answer because this helps prevent errors. In the first section of the Solutions Manual units are usually given, but in the Mathematica programs, units have been omitted as a simplification. Actually, Mathematica can work problems with units, and it can solve equations symbolically. These are things that you can try.

We are indebted to many physical chemists who have recommended problems and who have suggested improvements in this SOLUTIONS MANUAL. The following individuals made very useful suggestions as to how to improve the Mathematica™ solutions to Computer Problems: Ian Brooks (Wolfram Research), Carl W. David (U. Connecticut), Robert N. Goldberg (NIST), Mark R. Hoffmann (University of North Dakota), Andre Kuzniarek (Wolfram Research), W. Martin McClain (Wayne State University), Kathryn Tomasson (University of North Dakota), and Worth E. Vaughan (University of Wisconsin--Madison). We are also indebted to Peter Giunta who provided advice on word processing and Jennifer Yee who managed the production of the SOLUTIONS MANUAL at Wiley.

Robert J. Silbey
Robert A. Alberty
Moungi G. Bawendi

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SECOND SECTION: PROBLEMS THAT REQUIRE A PERSONAL COMPUTER WITH A MATHEMATICAL APPLICATION

PART ONE: THERMODYNAMICS

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1

Thermodynamic State of a Gas

1.1 The intensive state of an ideal gas can be completely defined by specifying (1) T, P, (2) T, $\bar{V}$, or (3) P, $\bar{V}$. The extensive state of an ideal gas can be specified in four ways. What are the combinations of properties that can be used to specify the extensive state of an ideal gas? Although these choices are deduced for an ideal gas, they apply to real gases.

SOLUTION

The extensive state is determined by (1) P, V, T, (2) P, n, T, (3) P, V, n, or (4) V, n, T.

1.2 The ideal gas law also represents the behavior of mixtures of gases at low pressures. The molar volume of the mixture is the volume of a mole of the mixture. The partial pressure of gas i in a mixture is defined as $y_i P$, where y_i is its mole fraction, and P is the total pressure. Ten grams of N_2 is mixed with 5 g of O_2 and held at 25 °C at 0.750 bar. (a) What are the mole fractions of N_2 and O_2? (b) What are the partial pressures of N_2 and O_2? (c) What is the volume of the ideal mixture?

SOLUTION

(a)
$$n_{N_2} = \frac{(10\text{ g})}{(28.013\text{ g mol}^{-1})} = 0.357\text{ mol}$$
$$n_{O_2} = \frac{(5\text{ g})}{(32.000\text{ g mol}^{-1})} = 0.156\text{ mol}$$
$$y_{N_2} = \frac{(0.357\text{ mol})}{(0.513\text{ mol})} = 0.696$$
$$y_{O_2} = \frac{(0.156\text{ mol})}{(0.513\text{ mol})} = 0.304$$

(b)
$$P_{N_2} = (0.696)(0.750\text{ bar}) = 0.522\text{ bar}$$
$$P_{O_2} = (0.304)(0.750\text{ bar}) = 0.228\text{ bar}$$

(c) $$V = nRT/P$$
$$= \frac{(0.513 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.750 \text{ bar}}$$
$$= 17.00 \text{ L}$$

1.3 A mixture of methane and ethane is contained in a glass bulb of 500 cm^3 capacity at 25 °C. The pressure is 1.25 bar, and the mass of gas in the bulb is 0.530 g. What is the average molar mass, and what is the mole fraction of methane?

SOLUTION

$$PV = nRT = \left(\frac{m}{M}\right)RT$$
$$M = \frac{mRT}{PV} = \frac{(0.530 \text{ g})(0.08315 \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(1.25 \text{ bar})(0.500 \text{ L})}$$
$$= 21.0 \text{ g mol}^{-1}$$

The molar mass of the mixture is a mole fraction weighted average of the molar masses of methane and ethane.

$$M = y_1 M_1 + y_2 M_2$$
$$21.0 = y_1\ 16.0 + (1 - y_1)30.0$$
$$14.0\ y_1 = 9.0$$
$$y_1 = \frac{9.0}{14.0} = 0.643$$

1.4 Nitrogen tetroxide is partially dissociated in the gas phase according to the reaction
$N_2O_4(g) = 2NO_2(g)$
A mass of 1.588 g of N_2O_4 is placed in a 500-cm^3 glass vessel at 298 K and dissociates to an equilibrium mixture at 1.0133 bar. (a) What are the mole fractions of N_2O_4 and NO_2? (b) What percentage of the N_2O_4 has dissociated? Assume the gases are ideal.

SOLUTION

There are two simultaneous equations because we know (1) the mass is equal to the sum of the masses of N_2O_4 and NO_2 and (2) the pressure of the mixture is equal to the sum of the partial pressures of the two gases.

$$m_{\text{total}} = 1.588 \text{ g} = m_{N_2O_4} + m_{NO_2} \qquad (1)$$

$$P_{\text{total}} = 1.0133 \text{ bar} = \frac{m_{N_2O_4}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(92 \text{ g mol}^{-1})(0.500 \text{ L})}$$

$$+\frac{m_{NO_2}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(46 \text{ g mol}^{-1})(0.500 \text{ L})}$$

$$= 0.5386\, m_{N_2O_4} + 1.0772\, m_{NO_2} \qquad (2)$$

$m_{NO_2} = 1.588 - m_{N_2O_4}$

Substituting this in equation (2) yields

$1.0133 = 0.5386\, m_{N_2O_4\,4} + 1.01772(1.588 - m_{N_2O_4})$

Thus

$m_{N_2O_4} = 1.295$ g or 0.01407 mol

$m_{NO_2} = 0.293$ g or 0.006370 mol

$n = 0.02044$ mol

(a) $$y_{N_2O_4} = \frac{0.01407 \text{ mol}}{0.02044 \text{ mol}} = 0.6884$$

$$y_{NO_2} = 1 - y_{N_2O_4} = 0.3116$$

(b) $$\% \text{ undissociated} = \frac{(0.01407 \text{ mol})(100)}{(1.588 \text{ g})/(92 \text{ g mol}^{-1})} = 81.51\ \%$$

% dissociated = 100 - 81.51 = 18.49%

1.5 Although a real gas obeys the ideal gas law in the limit as $P \to 0$, not all of the properties of a real gas approach the values for an ideal gas as $P \to 0$. The second virial coefficient of an ideal gas is zero, and so $dZ/dP = 0$ at all pressures. But calculate dZ/dP for a real gas as $P \to 0$.

SOLUTION

$Z = 1 + B'P + C'P^2 + \ldots$

$$\frac{dZ}{dP} = B' + 2\,C'P + \ldots$$

so that

$$\left(\frac{dZ}{dP}\right)_{P \to 0} = B'$$

This shows that a real gas does not behave like an ideal gas in all respects as $P \to 0$.

*1.6 Show how the second virial coefficient of a gas and its molar mass can be obtained by plotting P/ρ versus P, where ρ is the density of the gas. Apply this method to the following data on ethane at 300 K.

P/bar	1	10	20
$\rho/10^{-3}$ g cm^{-3}	1.2145	13.006	28.235

SOLUTION

$$P\bar{V} = RT + BP$$
$$PVM/m = RT + BP$$
$$P/\rho = RT/M + BP/M$$

Thus the intercept of the plot of P/ρ versus P is RT/M, and the slope is B/M. Plot P/ρ = 823.38, 768.88, 708.35 bar/g cm^{-3} versus P = 1, 10, 20 bar. The intercept is 829.44 bar/g cm^{-3} = RT/M, and so the molar mass of ethane is 30.07 g mol^{-1}. The slope is -6.056 cm^3 g^{-1} = B/M, and so B = (-6.056 cm^3 g^{-1})(30.07 g mol^{-1}) = -183 cm^3 mol^{-1}. This problem can also be solved using a computer program that calculates the intercept and slope by the method of least squares.

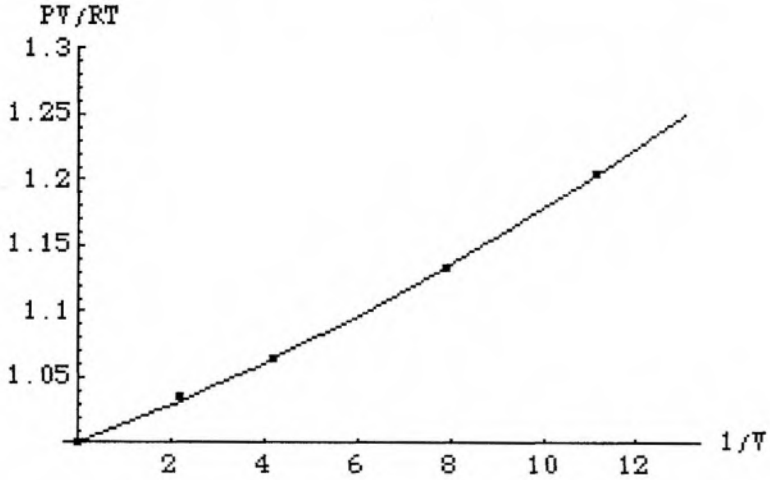
*1.7 Calculate the second and third virial coefficients of hydrogen at 0 °C from the fact that the molar volumes at 50.7, 101.3, 202.6, and 303.9 bar are 0.4634, 0.2386, 0.1271, and 0.09004 L mol^{-1}, respectively.

SOLUTION

$$P\bar{V}/RT = 1 + B/\bar{V} + C/\bar{V}^2 + \ldots$$

P/bar	50.7	101.3	202.6	303.9
$\bar{V}$/L mol^{-1}	0.4634	0.2386	0.1271	0.09004
$P\bar{V}/RT$	1.035	1.064	1.134	1.205
$(1/\bar{V})$/mol L^{-1}	2.158	4.191	7.868	11.106

The following plot has been prepared using *Mathematica* ™. In this calculation, the point $1/\bar{V} = 0$, $P\bar{V}/RT = 1$ was included.



In the plot labels, V is the molar volume. In making the plot, the point $P\bar{V}/RT = 1$ at $1/\bar{V} = 0$ has been included in obtaining a quadratic fit. the use of Fit in *Mathematica*™ yields $PV/RT = 1.001 + 0.0135(1/V) + 0.00043(1/V)^2$. Thus the second virial coefficient B is 0.0135 L mol^{-1} and the third virial coefficient is $4.35\text{x}10^{-4}$ L^2 mol^{-2}..

*1.8 The critical temperature of carbon tetrachloride is 283.1 °C. The densities in g/cm^3 of the liquid ρ_1 and vapor ρ_v at different temperatures are as follows:

t /°C	100	150	200	250	270	280
ρ_1	1.4343	1.3215	1.1888	0.9980	0.8666	0.7634
ρ_v	0.0103	0.0304	0.0742	0.1754	0.2710	0.3597

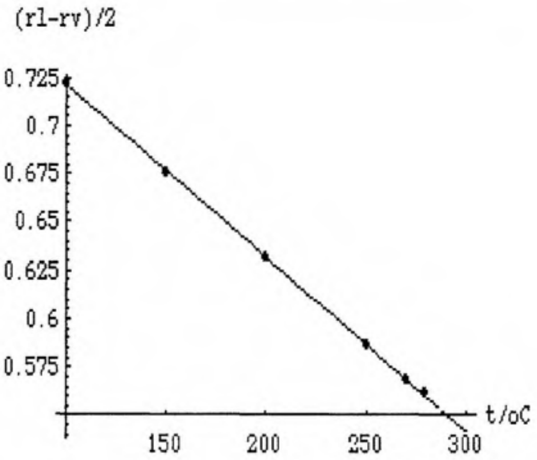
What is the critical molar volume of CCl_4? It is found that the mean of the densities of the liquid and vapor does not vary rapidly with temperature and can be represented by

$$\frac{\rho_1 + \rho_v}{2} = A + Bt$$

where A and B are constants. The extrapolated value of the average density at the critical temperature is the critical density. The molar volume $\bar{V}_c$ at the critical point is equal to the molar mass divided by the critical density.

SOLUTION

The following plot has been prepared using *Mathematica* ™.



Extrapolating $\frac{\rho_1 + \rho_v}{2}$ to T_c we obtain

$\rho_c = 0.557$ g cm^{-3}

$$\bar{V}_c = \frac{153.84 \text{ g mol}^{-1}}{0.557 \text{ g cm}^{-3}} = 276 \text{ cm}^3 \text{ mol}^{-1}$$

1.9 Show that for a gas of rigid spherical molecules, *b* in the van der Waals equation is four times the molecular volume times Avogadro's constant. If the molecular diameter of Ne is 0.258 nm (Table 17.4), approximately what value of *b* is expected?

SOLUTION

The molecular volume for a spherical molecule is

$$\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{\pi}{6} d^3$$

where *d* is the diameter. Since the center of a second spherical molecule cannot come within a distance *d* of the center of the first spherical molecule, the excluded volume per pair of molecules is $\frac{4}{3}\pi d^3$. The constant *b* in the van der Waals equation is the excluded volume per molecule times the Avogadro's constant

$$b = \left(\frac{4\pi}{6} d^3\right)N_A = \left(\frac{2}{3}\right)\pi d^3 N_A$$

For neon,

$$b = \left(\frac{2}{3}\right)\pi(0.258 \times 10^{-9} \text{ m})^3(6.02 \times 10^{23} \text{ mol}^{-1})$$
$$= 2.17 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Since 100 cm = 1 m, or 100 cm m^{-1} = 1, b can be expressed in $cm^3\ mol^{-1}$ by multiplying by $(100\ cm\ m^{-1})^3$.

$b = (2.17 \times 10^{-5}\ m^3\ mol^{-1})(100\ cm\ m^{-1})^3$

$= 21.7\ cm^3\ mol^{-1}$

1.10 What is the molar volume of *n*-hexane at 660 K and 91 bar according to (a) the ideal gas law and (b) the van der Waals equation? For *n*-hexane, T_c = 507.7 K and P_c = 30.3 bar

SOLUTION

(a)
$$\bar{V} = \frac{RT}{P}$$
$$= \frac{(0.08314\ L\ bar\ K^{-1}\ mol^{-1})(660\ K)}{91\ bar} = 0.603\ L\ mol^{-1}$$

(b)
$$a = \frac{27\,R^2T_c^2}{64\,P_c} = \frac{(27)(0.08314\ L\ bar\ K^{-1}\ mol^{-1})^2(507.7\ K)^2}{(64)(30.3\ bar)}$$
$$= 24.81\ L^2\ bar\ mol^{-2}$$

$$b = \frac{RT_c}{8\,P_c} = \frac{(0.08314\ L\ bar\ K^{-1}\ mol^{-1})(507.7\ K)}{8(30.3\ bar)} = 0.174\ L\ mol^{-1}$$

$$P = RT/(\bar{V}_c - b) - a/\bar{V}^2$$
$$91\ bar = \frac{(0.08314)(660\ K)}{(\bar{V} - 0.174)} - \frac{24.81}{\bar{V}^2}$$

Rather than solving a cubic equation, substituting successive values of $\bar{V}$ shows that $\bar{V} = 0.39\ L\ mol^{-1}$.

1.11 Derive the expressions for van der Waals constants a and b in terms of the critical temperature and pressure; that is, derive equations 1.32 and 1.33 from 1.29 and 1.30.

SOLUTION

Equations 1.29 and 1.30 may be written

$$RT_c/(\bar{V}_c - b)^2 = 2a/(\bar{V}_c^3) \qquad (1)$$

$$2RT_c/(\bar{V}_c - b)^3 = 6a/\bar{V}_c^{-4} \qquad (2)$$

Division of the first equation by the second yields

$\bar{V}_c = 3b$ (3)

Substitution of this expression in equation 1 yields

$T_c = 8a/27Rb$ (4)

Substitution of equations 3 and 4 in equation 1.31 yields

$P_c = a/27b^2$ (5)

Since there are three relations (equations 3-5) between the van der Waals constants and the critical constants, a and b may be expressed in terms of T_c and P_c or T_c and $\bar{V}_c$. Critical pressures are generally known more accurately than critical volumes, and so a and b are generally calculated using data on the critical temperature and pressure.

1.12 Calculate the second virial coefficient of methane at 300 K and 400 K from its van der Waals constants, and compare these results with Fig. 1.9.

SOLUTION

For methane $a = 2.283$ L^2 bar mol^{-2} and $b = 0.04278$ L mol^{-1}. From equation 1.28, the second virial coefficient at 300 K is

$$B = b - a/RT = 0.04278 - \frac{2.283}{(0.08314)(300)}$$

$$= -0.048 \text{ L mol}^{-1}$$

At 400 K, $B = -0.026$

Fig. 1.9 yields - 0.040 L mol^{-1} at 300 K and - 0.020 L mol^{-1} at 400 K.

*1.13 You want to calculate the molar volume of O_2 at 298.15 K and 50 bar using the van der Waals equation, but you don't want to solve a cubic equation. Use the first two terms of equation 1.26 to obtain an approximate solution. The van der Waals constants of O_2 are $a = 0.138$ Pa m^6 mol^{-1} and $b = 31.8 \times 10^{-6}$ m^3 mol^{-1}. What is the molar volume in L mol^{-1}?

SOLUTION

$$\frac{P\bar{V}}{RT} = 1 + \frac{1}{RT}(b - \frac{a}{RT})P$$

$$\bar{V} = \frac{RT}{P}\left[1 + \frac{1}{RT}(b - \frac{a}{RT})P\right]$$

$$= \frac{RT}{P} + b - \frac{a}{RT}$$

$$= \frac{(8.31451 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{50 \times 10^5 \text{ Pa}} + 31.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$- \frac{0.138 \text{ Pa m}^6 \text{ m}^{-2}}{(8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$= (495.8 \times 10^{-6} + 31.8 \times 10^{-6} - 55.7 \times 10^{-6})$ m^3 mol^{-1}

$= 471.9 \times 10^{-6}$ m^3 mol^{-1}

$= 0.4719$ L mol^{-1}

If you have a computer program for solving polynomials, it can be used to check this approximation method.

1.14 The isothermal compressibility κ of a gas is defined in problem 1.17, and its value for an ideal gas is shown to be $1/P$. Use implicit differentiation of V with respect to P at constant T to obtain the expression for the isothermal compressibility of a van der Waals gas. Show that in the limit of infinite volume, the value for an ideal gas is obtained.

SOLUTION

The van der Waals equation can be written

$nRT = PV - nPb + n^2a/V - n^3ab/V^2$

Implicit differentiation with respect to P at constant T yields

$V + P(\partial V/\partial P)_T - nb - (n^2a/V^2)(\partial V/\partial P)_T + (2n^3ab/V^3)(\partial V/\partial P)_T = 0$

Solving for $(\partial V/\partial P)_T$ yields

$$(\partial \text{V}/\partial \text{P})_\text{T} = \frac{nb - V}{P - n^2a/V^2 + 2n^3ab/V^3}$$

Thus the isothermal compressibility of a van der Waals gas is given by

$$\kappa = \frac{V - nb}{PV - n^2a/V + 2n^3ab/V^2}$$

When V is very large, this expression for the isothermal compressibility reduces to $\kappa = V/PV = 1/P$ as expected.

1.15 Calculate the second and third virial coefficients of O_2 from its van der Waals constants in Table 1.3.

SOLUTION

The van der Waals constants for O_2 are a = 1.378 L^2 bar mol^{-2} and b = 0.03183 L mol^{-1}.

We need the conversion factor between m^3 and L. Since a liter is 10^3 cm^3 and a cubic meter is 100^3 cm^3, the conversion factor is 10^3 L m^{-3}.

The second virial coefficient B is given by

$B = b - a/RT = .03183/10^3 - 1.378/(.08315 \times 298.15 \times 10^3) = -0.0000238$ m^3 mol^{-1}

The expected value is -0.0000161 m^3 mol^{-1}.

The third virial coefficient is given by
$C = b^2 = (.03183/10^3)^2 = 1.01\text{x}10^{-9}\ \text{m}^6\ \text{mol}^{-2}$.

The expected value is $1.2\text{x}10^{-9}\ \text{m}^6\ \text{mol}^{-2}$.

1.16 Calculate the critical properties for ethane using the van der Waals constants in Table 1.3.

SOLUTION

The critical properties for molecular oxygen are given by

$$\bar{V}_{\text{c}} = 3b = 3(.0635\ \text{L mol}^{-1}) = 0.1914\ \text{L mol}^{-1}$$

$$T_{\text{c}} = \frac{8a}{27Rb} = \frac{8(5.562\ \text{L}^2\ \text{bar mol}^{-2})}{27(0.038\ \text{L mol}^{-1})(0.083145\ \text{l bar K}^{-1}\ \text{mol}^{-1})} = 310.671\ \text{K}$$

$$P_{\text{c}} = \frac{a}{27b^2} = \frac{5.562\ \text{L}^2\ \text{bar mol}^{-2}}{27(0.0638\ \text{L mol}^{-1})^2} = 50.609\ \text{bar}$$

1.17 The cubic expansion coefficient α is defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and the isothermal compressibility is defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

Calculate these quantities for an ideal gas.

SOLUTION

$V = nRT/P$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\alpha = \frac{1}{T}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$\kappa = \frac{nRT}{VP^2} = \frac{1}{P}$$

1.18 What is the equation of state for a liquid for which the coefficient of cubic expansion α and the isothermal compressibility κ are constant?

SOLUTION

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P$$

$$= \alpha V \mathrm{d}T - \kappa V \mathrm{d}P$$

$$\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = \alpha \int_{T_1}^{T_2} \mathrm{d}T - \kappa \int_{P_1}^{P_2} \mathrm{d}P$$

$$\ln(V_2/V_1) = \alpha(T_2 - T_1) - \kappa(P_2 - P_1)$$

The indefinite integral and its exponential form are

$$\ln V = \alpha T - \kappa P + \text{const.}$$

$$V = C\, \mathrm{e}^{\alpha T}\, \mathrm{e}^{-\kappa P}$$

where C is a constant.

1.19 For a liquid the cubic expansion coefficient α is nearly constant over a narrow range of temperature. Derive the expression for the volume as a function of temperature and the limiting form for temperatures close to T_0.

SOLUTION

$$\int_{V_0}^{V} \frac{\mathrm{d}V}{V} = \alpha \int_{T_0}^{T} \mathrm{d}T$$

$$\ln \frac{V}{V_0} = \alpha\,(T - T_0)$$

$$\mathrm{V} = \mathrm{V}_0\, \mathrm{e}^{\alpha(T - T_0)}$$

If $\alpha(T - T_0) << 1$,

$$V = V_0[1 + \alpha(T - T_0)]$$

1.20 (a) Derive the expressions for $(\partial P/\partial V)_T$ and $(\partial P/\partial T)_V$ for a gas that has the following equation of state:

$$P = \frac{nRT}{V - nb}$$

(b) Show that $(\partial^2 P/\partial V \partial T) = (\partial^2 P/\partial T \partial V)$. These are referred to as mixed partial derivatives.

SOLUTION

(a) $$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-\,nRT}{(V - nb)^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb}$$

(b) $$\left(\frac{\partial^2 P}{\partial V \partial T}\right) = \frac{-nR}{(V-nb)^2}$$

$$\left(\frac{\partial^2 P}{\partial T \partial V}\right) = \frac{-nR}{(V-nb)^2}$$

1.21 Assuming that the atmosphere is isothermal at 0 °C and that the average molar mass of air is 29 g mol^{-1}, calculate the atmospheric pressure at 20,000 ft above sea level.

SOLUTION

$h = (2.0 \text{ x } 10^4 \text{ ft})(12 \text{ in ft}^{-1})(2.54 \text{ cm in}^{-1})(10^{-2} \text{ m cm}^{-1})$
$= 6096 \text{ m}$

$P = P_o \, e^{-gMh/RT}$

$$P = (1.013 \text{ bar}) \exp\left[\frac{-(9.8 \text{ m s}^{-2})(29 \text{ x } 10^{-3} \text{ kg mol}^{-1})(6096 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K})}\right] = 0.472 \text{ bar}$$

1.22 Calculate the pressure and composition of air on the top of Mt. Everest assuming the atmosphere has a temperature of 0 °C independent of altitude (h = 29,141 ft). Assume that air at sea level is 20% O_2 and 80% N_2.

SOLUTION

$h = (29{,}141 \text{ ft})(12 \text{ in ft}^{-1})(2.54 \text{ cm in}^{-1})(0.01 \text{ m cm}^{-1}) = 8{,}882 \text{ m}$

For O_2, $P = (0.2 \text{ bar}) \exp(-9.8 \text{ x } 32 \text{ x } 10^{-3} \text{ x } 8882/(8.314 \text{ x } 273))$

$= 0.059 \text{ bar}$

For N_2, $P = (0.8 \text{ bar}) \exp(-9.8 \text{ x } 28 \text{ x } 10^{-3} \text{ x } 8882/(8.314 \text{ x } 273))$

$= 0.274 \text{ bar}$

The total pressure is 0.333 bar, $y_{O_2} = 0.177$ and $y_{N_2} = 0.823$.

1.23 (a) 98.1 kPa, (b) 9810 MPa, (c) 98.1 cm^2

1.24 (a) 0.02479 m^3, (b) 0.02560 m^3, (c) 0.7747, 0.1937, 0.0317

1.25 0.835

1.26 $B = y_1^2 B_{11} + 2y_1y_2 B_{12} + y_2^2 B_{22}$

1.27 276 $cm^3\ mol^{-1}$

1.28 $-1.96 \times 10^{-3}\ bar^{-1}$, $-0.60 \times 10^{-4}\ bar^{-1}$

1.29 $C = b^2$ and $D = b^3$

1.30 (a) 20.1 bar, (b) 1642 bar, (c) 2776 bar

1.31 99.8 bar, 152 bar

1.32 (a) 155 bar, (b) 88.6 bar

1.33 $V_2 = V_1 \exp[-\kappa (P_2 - P_1)]$

1.34 $\alpha = 1/T(1 + bP/RT)$

$\kappa = 1/P(1 + bP/RT)$

1.35 (a) 6.93×10^{-2} L mol^{-1}, (b) 8.62×10^{-2} L mol^{-1}.

1.36 0.843 bar

1.37 3.27×10^{-9} bar, $y_{O_2} = 0.015$, $y_{N_2} = 0.985$

1.38 $M = y_A M_A + y_B M_B$

2

First Law of Thermodynamics

2.1 How high can a person (assume a weight of 70 kg) climb on one ounce of chocolate, if the heat of combustion (628 kJ) can be converted completely into work of vertical displacement?

SOLUTION

$$w = mgh$$

$$h = \frac{w}{gm} = \frac{628\ 000\ \text{J}}{(9.806\ \text{m s}^{-2})(70\ \text{kg})} = 914\ \text{m}$$

2.2 A mole of sodium metal is added to water. How much work is done on the atmosphere by the subsequent reaction if the temperature is 25 °C?

SOLUTION

$$\text{Na(s)} + \text{H}_2\text{O(1)} = \text{NaOH(soln)} + \tfrac{1}{2}\ \text{H}_2\text{(g)}$$

$$\bar{V} = \frac{RT}{P} = \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{(101325\ \text{Pa})}$$
$$= 0.0245\ \text{m}^3\ \text{mol}^{-1}$$

$$w = -P\Delta\bar{V} = -(101\ 325\ \text{Pa})(0.0123\ \text{m}^3\ \text{mol}^{-1})$$
$$= -1.24\ \text{kJ mol}^{-1}$$

2.3 You want to heat 1 kg of water 10 °C, and you have the following four methods under consideration. The specific heat capacity of water is 4.184 J K^{-1} g^{-1}.

(a) You can heat it with a mechanical eggbeater that is powered by a 1 kg mass on a rope over a pulley. How far does the mass have to descend in the earth's gravitational field to supply enough work?

(b) You can send 1 ampere through a 100 Ω resistor. How long will it take?

(c) You can send the water through a solar collector that has an area of 1 m^2. How long will it take if the sun's intensity on the collector is 4 J cm^{-2} min^{-1}?

(d) You can make a charcoal fire. The heat of combustion of graphite is -393 kJ mol^{-1}. That is, 12 g of graphite will produce 393 kJ of heat when it is burned to $CO_2(g)$ at constant pressure. How much charcoal will you have to burn?

SOLUTION:

(a) $(1000\text{ g})(4.184\text{ J K}^{-1}\text{ g}^{-1})(10\text{ K}) = 4.184 \times 10^4\text{ J}$

$mg\Delta h = (1\text{ kg})(9.8\text{ m s}^{-2})\Delta h$

$$\Delta h = \frac{4.184 \times 10^4}{9.8} = 4269\text{ m}$$

(b) $I^2Rt = 4.184 \times 10^4\text{ J} = (1\text{A})^2(100\ \Omega)t$

$$t = \frac{4.184 \times 10^4}{100} = 418.4\text{ s} = 6.97\text{ minutes}$$

(c) $4.184 \times 10^4\text{ J} = (4.0\text{ J cm}^{-2}\text{ min}^{-1})(100\text{ cm})^2\ t$

$$t = \frac{4.184 \times 10^4}{4 \times 10^4} = 1.05\text{ minutes}$$

(d) $4.184 \times 10^4\text{ J} = (393 \times 10^3\text{ J})\dfrac{m}{12}$

$$m = \frac{12(4.184 \times 10^4)}{393 \times 10^3} = 1.28\text{ grams}$$

2.4 Show that the differential df is inexact.

$df = dx - (x/y)dy$

Thus the integral $\int df$ depends on the path. However, we can define a new function g by

$dg = (1/y)df$

which has the property that dg is exact. Show that dg is exact, so that $\oint dg = 0$. In this case y is referred to as an integrating factor.

SOLUTION

To determine whether df is exact take the cross derivatives

$M(x,y) = 1;\ (\partial M/\partial y)_x = 0$

$N(x,y) = -\ x/y,\ \ (\partial N/\partial x)_y = -\ 1/y$

Since $(\partial M/\partial y)_x \neq (\partial N/\partial x)_y$, df is inexact.

The new differential is given by

$dg = (1/y)\ dx - (x/y^2)dy$

Now take the cross derivatives.

$M = 1/y,\ (\partial M/\partial y)_x = -1/y^2$

$N = -\ x/y^2,\ (\partial N/\partial x)_y = -1/y^2$

Since $(\partial M/\partial y)_x = (\partial M/\partial x)_y$, dg is exact.

2.5 Show that the function $f(x,y)$ defined by

$df(x,y) = (x + 2y)dx - xdy$

is inexact. Test to see whether the integrating factor $1/x^3$ makes it an exact differential.

SOLUTION

The function is exact if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Taking the two mixed partial derivatives yields

$$\left[\frac{\partial (x + 2y)}{\partial y}\right]_x = 2$$

$$\left[\frac{\partial (-x)}{\partial x}\right]_y = -1$$

showing that the function *f(x,y)* is inexact.

Multiplying by the integrating factor yields

$$\frac{df(x,y)}{x^3} = \frac{x + 2y}{x^3}\, dx - \frac{1}{x^2}\, dy$$

Taking the two mixed partial derivatives yields

$$\left[\frac{\partial \left(\frac{x + 2y}{x^3}\right)}{\partial y}\right]_x = \frac{2}{x^3}$$

$$\left[\frac{\partial \left(\frac{-1}{x^2}\right)}{\partial x}\right]_y = \frac{2}{x^3}$$

Since the mixed partial derivatives are equal, $f(x,y)/x^3$ is exact.

2.6 Show that the function defined by

$df(x,y) = (y^2 - xy)dx - x^2dy$

is inexact. Test the integrating factor $1/xy^2$ to see whether it produces an exact differential.

SOLUTION

The function is exact if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Taking the two mixed partial derivatives yields

$$\left[\frac{\partial (y^2 - xy)}{\partial y}\right]_x = 2y - x$$

$$\left[\frac{\partial (-x^2)}{\partial x}\right]_y = -2x$$

showing that the function *f(x,y)* is inexact.

Multiplying by the integrating factor yields

$$\frac{df(x,y)}{xy^2} = \left(\frac{1}{x} - \frac{1}{y}\right)dx - \frac{x}{y^2}\, dy$$

Taking the partial derivatives yields

$$\left[\frac{\partial\left(\frac{1}{x}-\frac{1}{y}\right)}{\partial y}\right]_x = \frac{1}{y^2}$$

$$\left[\frac{\partial\left(\frac{x}{y^2}\right)}{\partial x}\right]_y = \frac{1}{y^2}$$

Since the mixed partial derivatives are equal, $f(x,y)/xy^2$ is exact.

2.7 What are the partial derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial y)_x$ of the following functions.

(a) $z = xy$, (b) $z = x/y$, (c) $z = \ln(xy)$, (d) $z = \ln(x/y)$, and (e) $z = \exp(xy)$.

SOLUTION

(a) $\left(\frac{\partial z}{\partial x}\right)_y = y;\quad \left(\frac{\partial z}{\partial y}\right)_x = x$

(b) $\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{y};\quad \left(\frac{\partial z}{\partial y}\right)_x = \frac{-x}{y^2}$

(c) $z = \ln x + \ln y;\ \left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{x};\quad \left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{y}$

(d) $z = \ln x - \ln y;\ \left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{x};\quad \left(\frac{\partial z}{\partial y}\right)_x = \frac{-1}{y}$

(e) $\left(\frac{\partial z}{\partial x}\right)_y = ye^{xy};\ \left(\frac{\partial z}{\partial y}\right)_x = xe^{xy}$

2.8 (a) The surface tension of water at 25 °C is 0.072 N m^{-1}. How much work is required to form a surface 100 m by 100 m? (b) The force on a wire is due to a 75 kg person in the earth's gravitational field. If the wire stretches 1 m, how much work is done on the wire? (c) A gas expands 1 L against a constant external pressure of 1 bar. How much work is done on the gas?

SOLUTION

(a) $w = (0.072 \text{ N m}^{-1})(100 \text{ m})^2 = 720 \text{ J}$
(b) $w = (9.8 \text{ m s}^{-2})(75 \text{ kg})(1 \text{ m}) = 735 \text{ J}$

(c) $w = -P\Delta V = -(1 \text{ bar})(1 \text{ L}) = (10^5 \text{ Pa})(10^{-3} \text{ m}^3) = -100 \text{ Pa m}^3 = -100 \text{ J}$

2.9 Over narrow ranges of temperature and pressure, the differential expression for the volume of a fluid as a function of temperature and pressure can be integrated to obtain

$V = K e^{\alpha T} e^{-\kappa P}$

(α and κ are defined in problem 1.17). Show that V is a state function.

SOLUTION

The test of a state function is that it forms exact differentials. For an exact differential the mixed second derivatives are equal.

$$\left(\frac{\partial V}{\partial T}\right)_P = K e^{-\kappa P} e^{\alpha T} \alpha$$

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T = K e^{\alpha T} e^{-\kappa P} (-\kappa\alpha)$$

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_T = K e^{\alpha T} e^{-\kappa P} (-\kappa)$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = K e^{\alpha T} e^{-\kappa P} (-\kappa\alpha)$$

Thus V for a substance that can be described in this way is a state function.

2.10 One mole of nitrogen at 25 °C and 1 bar is expanded reversibly and isothermally to a pressure of 0.132 bar. (a) How much work w is done on the gas? (b) How much work is done on the gas if it is expanded against a constant pressure of 0.132 bar?

SOLUTION

(a) $w = RT \ln(P_2/P_1)$

$= (8.314 \text{ J K}^{-1})(298.15 \text{ K}) \ln 0.132$

$= - 5.03 \text{ kJ mol}^{-1}$

(b) $$\bar{V}_1 = RT/P_1 = \frac{(8.314)(298.15)}{10^5} = 0.0248 \text{ m}^3 \text{ mol}^{-1}$$

$$\bar{V}_2 = \frac{(8.314)(298.15)}{(0.132)(10^5)} = 0.188 \text{ m}^3 \text{ mol}^{-1}$$

$$w = - P\Delta\bar{V} = - (0.132 \times 10^5)(0.188 - 0.0248)$$

$$= - 2.15 \text{ kJ mol}^{-1}$$

2.11 (a) Derive the equation for the work of reversible isothermal expansion of a van der Waals gas from V_1 to V_2. (b) A mole of CH_4 is expanded reversibly from 1 L to 50 L at 25 °C. Calculate the work in joules assuming (1) the gas is ideal, (2) the gas obeys the van der Waals equation. For CH_4 (g), $a = 2.283 \text{ L}^2 \text{ bar mol}^{-2}$, $b = 0.04278 \text{ L mol}^{-1}$.

SOLUTION